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December 10, 2010

Silicon containing polymers and composites 2010  
San Diego, CA, United States  
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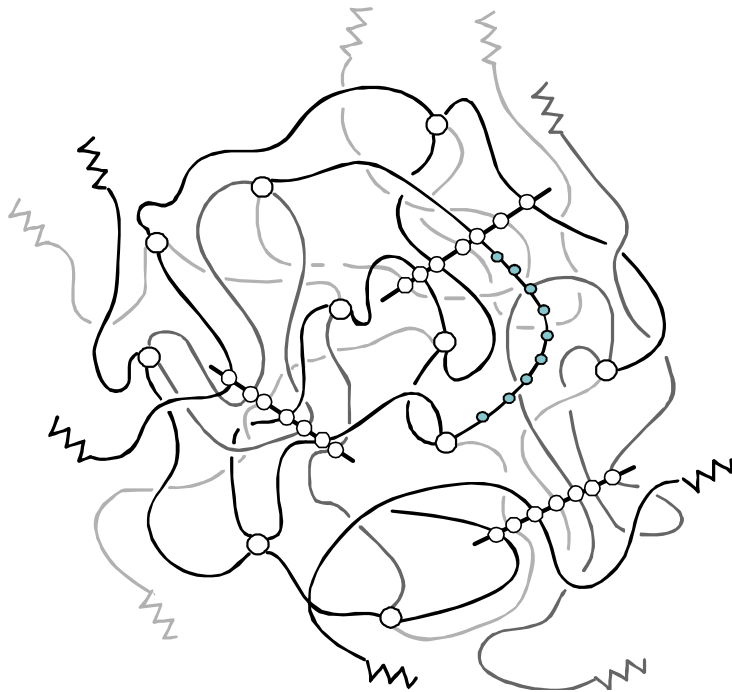
## Solid State NMR Investigations of Chain Dynamics and Network Order in Model Poly(dimethylsiloxane) Elastomers



James P. Lewicki, Brian P. Mayer, Thomas S. Wilson, Sarah C. Chinn & Robert S. Maxwell

Silicon containing polymers and composites. San Diego, CA Dec. 2010

# Characterization of siloxane networks



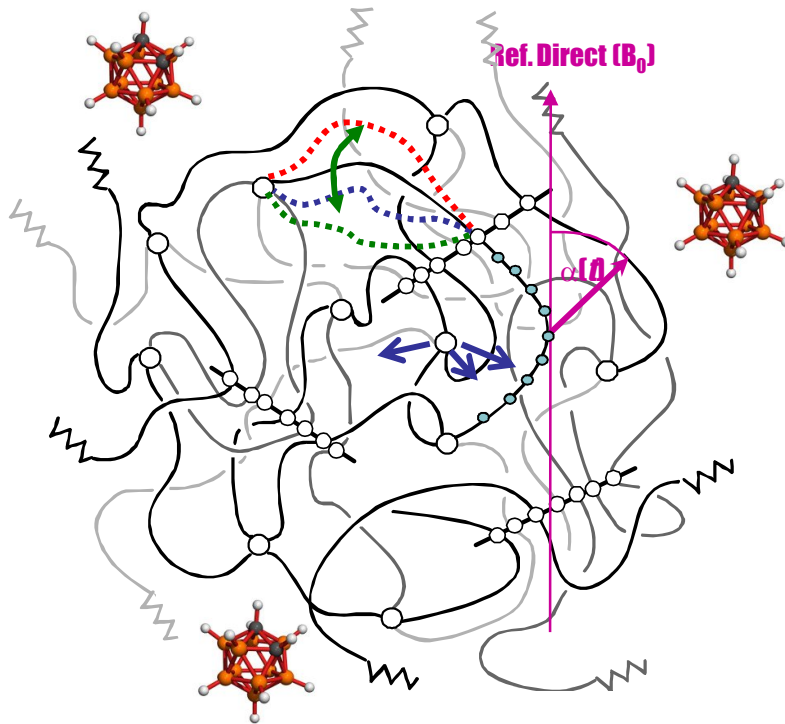
- The macroscopic properties of crosslinked siloxane elastomers are a consequence of the **chemical structure, local segmental, long range order & architecture** of the networks.
- **Side groups, crosslink sites, physical entanglements, free chain ends, end-end chain length(s) & filler phases all influence the overall network properties**

■ *Standard spectroscopic, mechanical and chromatographic techniques can only reveal so much about chemically cross linked, somewhat intractable networks*

How then can we better characterize & understand structure-property relationships in such materials?

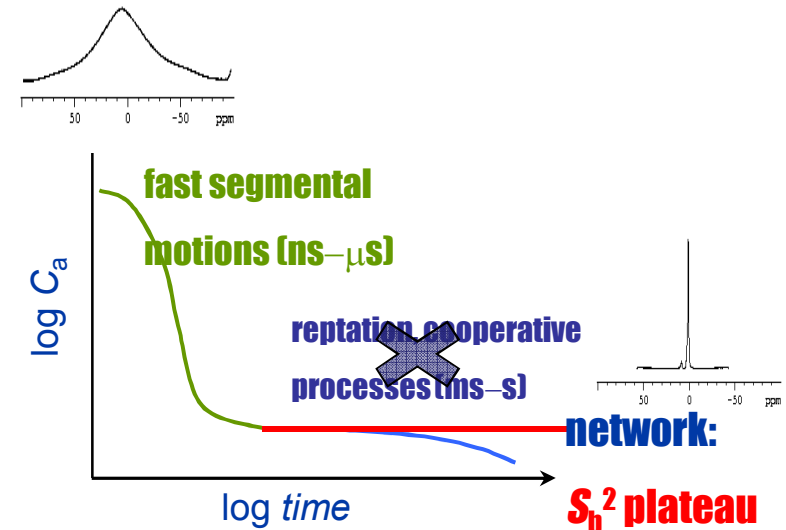
# NMR provides an indirect quantification of P(MP) via effect of network topology on segmental dynamics

## Chain dynamics



$n$  entangled & cross-linked chains,  $N$  segments each

## Effect on autocorrelation function and NMR spectra

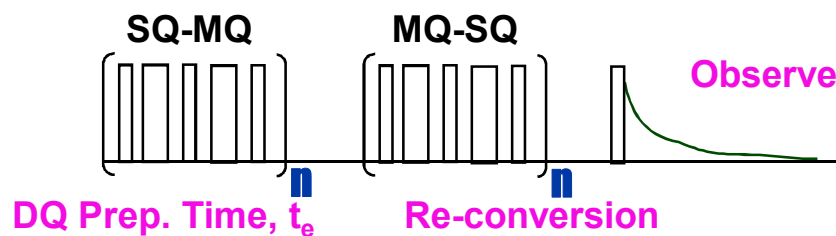


$$S_b = k \frac{\langle \Omega_d \rangle}{\langle \Omega_d \rangle_{static}} = \frac{3}{5} \frac{r^2}{N}$$

NMR can provide a way to characterize network structure and how structure changes with time.

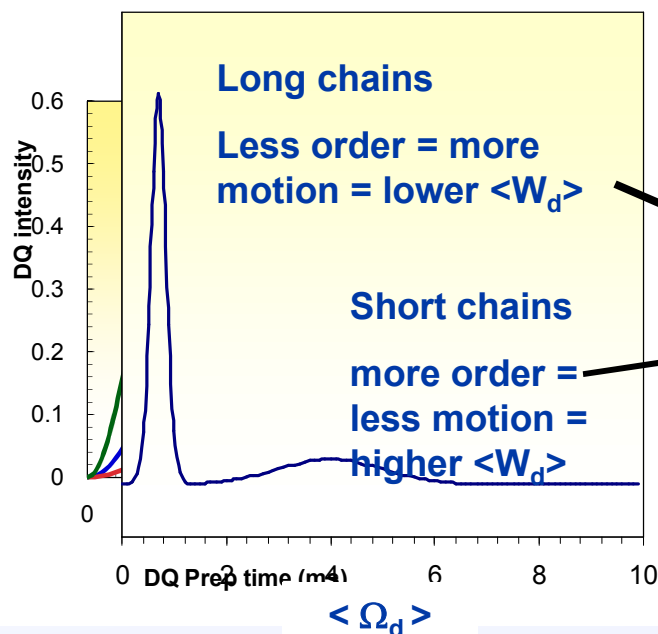
# For siloxane systems, static $^1\text{H}$ MQ-NMR provides direct access to these distributions in segmental dynamics.

## Pulse sequence

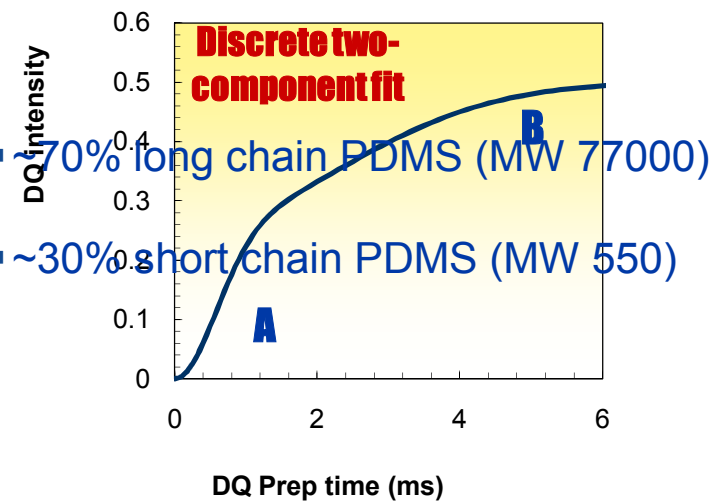


$$\Rightarrow I_{MQ}(\tau_e) = \sum 0.5 * X_i * \left(1 - \exp\left(-B \langle \Omega_d \rangle_i^2 \tau_e^2\right)\right)$$

## Normalized DQ growth curves



## Complex or highly filled network

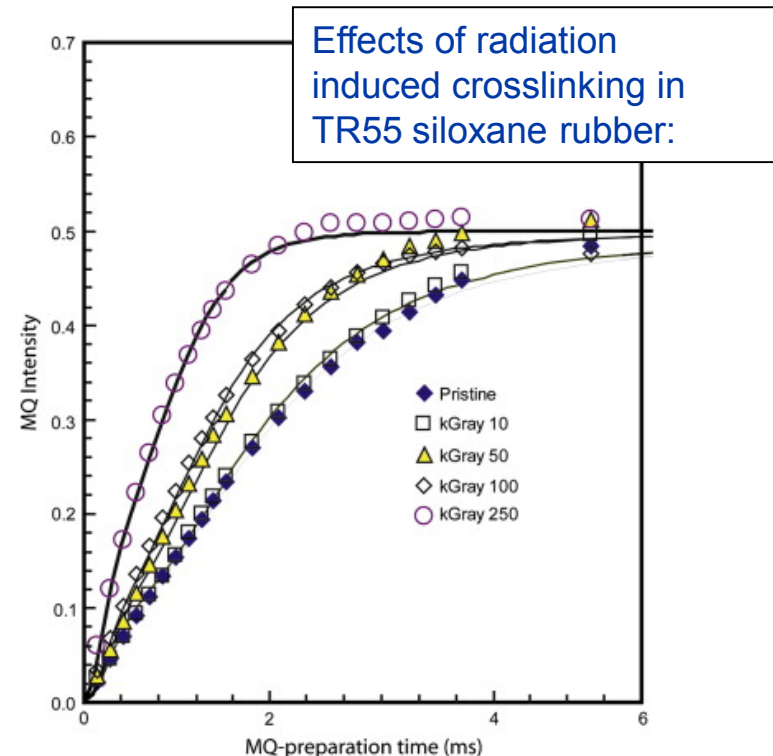
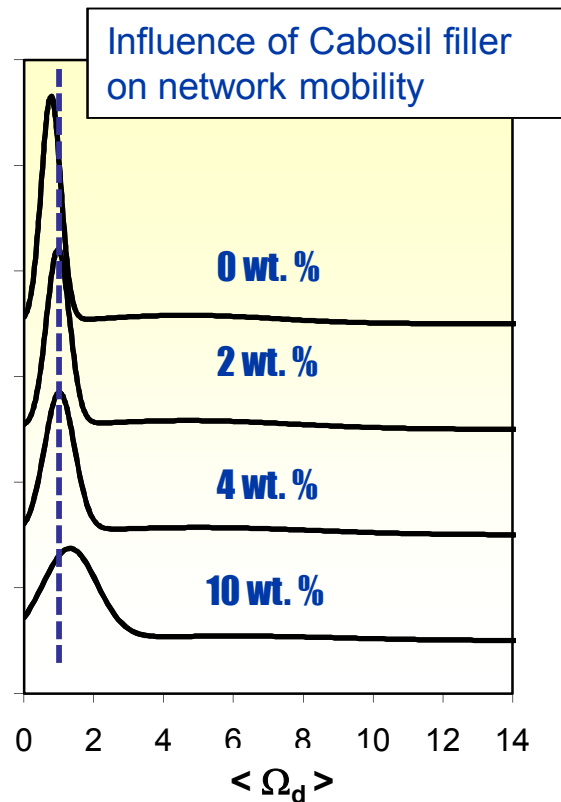


Maxwell, et al, *Macromolecules* **2005**, Saalwächter, K. *Prog. NMR Spect.* **2007**, 51, 1



# The current 'state of play'

- For ~5 years now, MQ-NMR has been used as a tool for probing siloxane network behavior to great effect:



Maxwell, Chinn et al. Polymer Degradation and Stability 94 (2009) 456–464

However, what are some of the unanswered questions, uncertainties & limitations?

# What are the limits and what don't we understand?

- How do additional components (fillers etc) & complex network architectures affect RDC distribution curves and how do we relate NMR data from complex systems back to valid descriptions of overall network structure?
- In order to extract MW distributions for RDC distributions we make several empirical assumptions – are the current assumptions we make valid and can we test these?
- *We don't fully yet understand how network topology translates itself into RDC distributions and if we are simply assuming too much, having started with the most complex of systems*

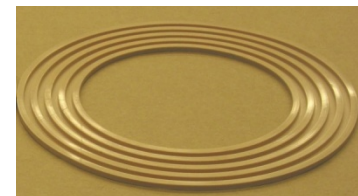
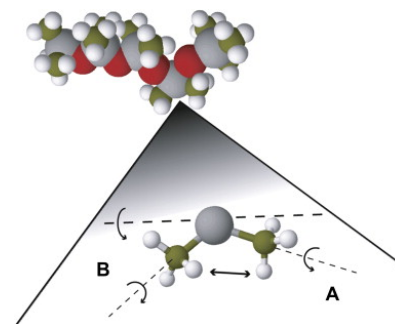
How can we address these issues and answer some of these questions definitively?





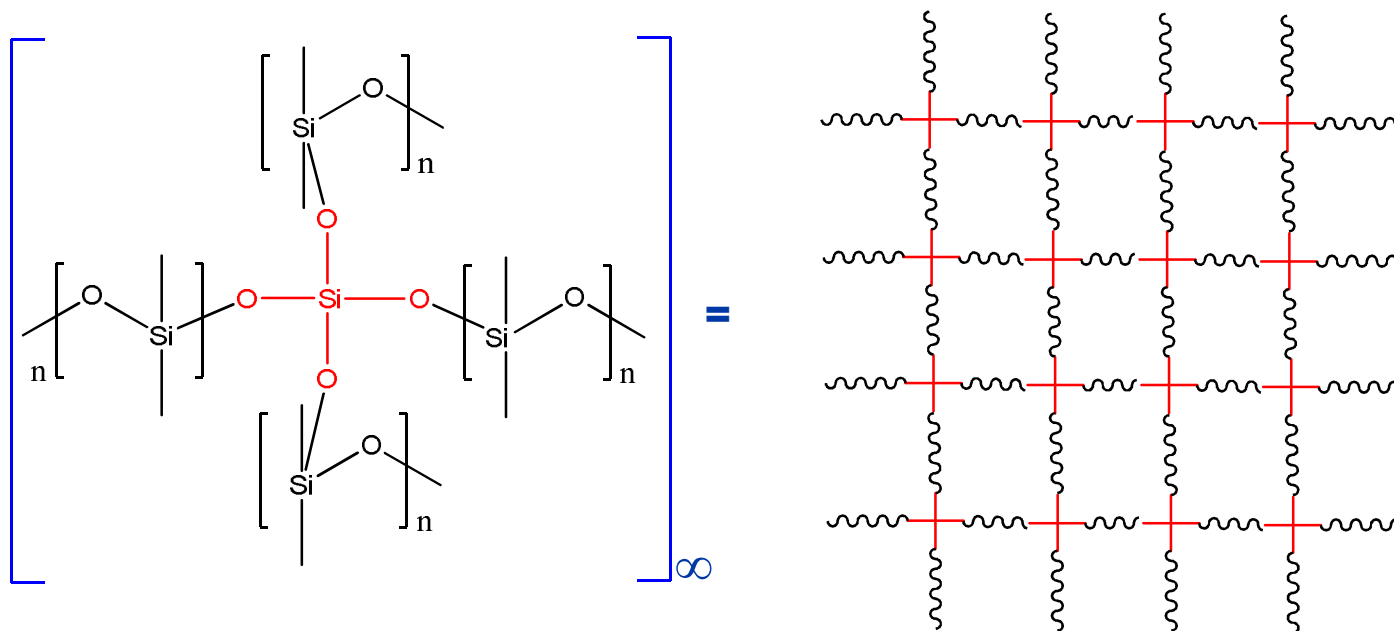
# Our Strategy: Experimental model networks

- Formulate a matrix of well defined PDMS networks incorporating the individual component architectures and functionalities that contribute to real-world network properties
- Define and characterize the influence of each variable using MQ-NMR methodology
- Feed the component data back into a model of a complex, multi-component network system & compare with existing data on real-world Siloxane elastomer systems



# Current model systems based on Sn catalyzed condensation cure

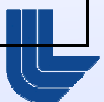
- Monomodal, tetra-functional, end-crosslinked condensation cured. Variable end-end chain length



This chemistry is not ideal, but the stoichiometry is controlled to limit excess TEOS condensation

# The 1<sup>st</sup> generation model matrix

Code	Base OH term. PDMS Molar mass	TEOS crosslinker level (g)	Network type
8KM	8 KDa	0.065	Monomodal
10KM	9.6 KDa	0.054	Monomodal
32KM	32.3 KDa	0.032	Monomodal
54KM	54.4 KDa	0.019	Monomodal
68KM	68.4 KDa	0.015	Monomodal
133KM	132.6 KDa	0.008	Monomodal
8_32KB	8 KDa, 32.3 KDa	0.081	BiModal (50:50)
8_54KB	8 KDa, 54.4 KDa	0.075	BiModal (50:50)
8_68KB	8 KDa, 68.4 KDa	0.073	BiModal (50:50)
8_133KB	8 KDa, 132.6 KDa	0.069	BiModal (50:50)
8_133K10B	8 KDa, 132.6 KDa	0.0137	BiModal (10:90)
8_133K25B	8 KDa, 132.6 KDa	0.038	BiModal (25:75)
8_133K75B	8 KDa, 132.6 KDa	0.099	BiModal (75:25)
8_133K90B	8 KDa, 132.6 KDa	0.118	BiModal (90:10)
68KF20	68.4 KDa, (14.1 KDa mono OH)	0.0075	Monomodal 20% free chain ends
68KF10	68.4 KDa, (14.1 KDa mono OH)	0.0075	Monomodal 10% free chain ends
68KF5	68.4 KDa, (14.1 KDa mono OH)	0.0075	Monomodal 5% free chain ends
68KF1	68.4 KDa, (14.1 KDa mono OH)	0.0075	Monomodal 1% free chain ends



Results & discussion

# CHARACTERIZATION OF MONO, BI-MODAL AND FREE CHAIN END NETWORKS

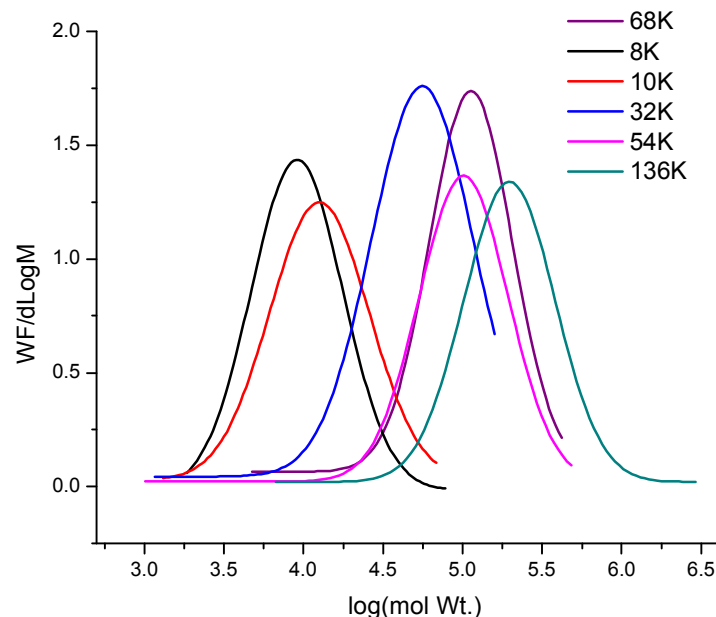
**Three case studies of model PDMS networks**



# PDMS precursors selected for model networks

In these first generation model systems, linear OH terminated PDMS polymers were selected over a MW range from below entanglement ( $\sim 12$  KDa) to well above:

8 Kda ; 10 KDa ; 31 KDa ; 51 KDa; 68 KDa ; 133 KDa



Polymer	Viscosity (cst.)	Ave $M_n$	Ave. $M_w$	PDI
8K	65	8076, 6%err	11345, 4%err	1.406, 2%err
10K	90-150	9247, 6%err	14328, 7%err	1.549, 1%err
32K	750	30592, 10%err	59190, 5%err	1.945, 9%err
54K	1800-2200	51208, 10%err	107371, 4%err	2.107, 7%err
68K	3500	68370, 4%err	116083, 2%err	1.691, 2%err
133K	50,000	133848, 2%err	232278, 3%err	1.736, 3%err

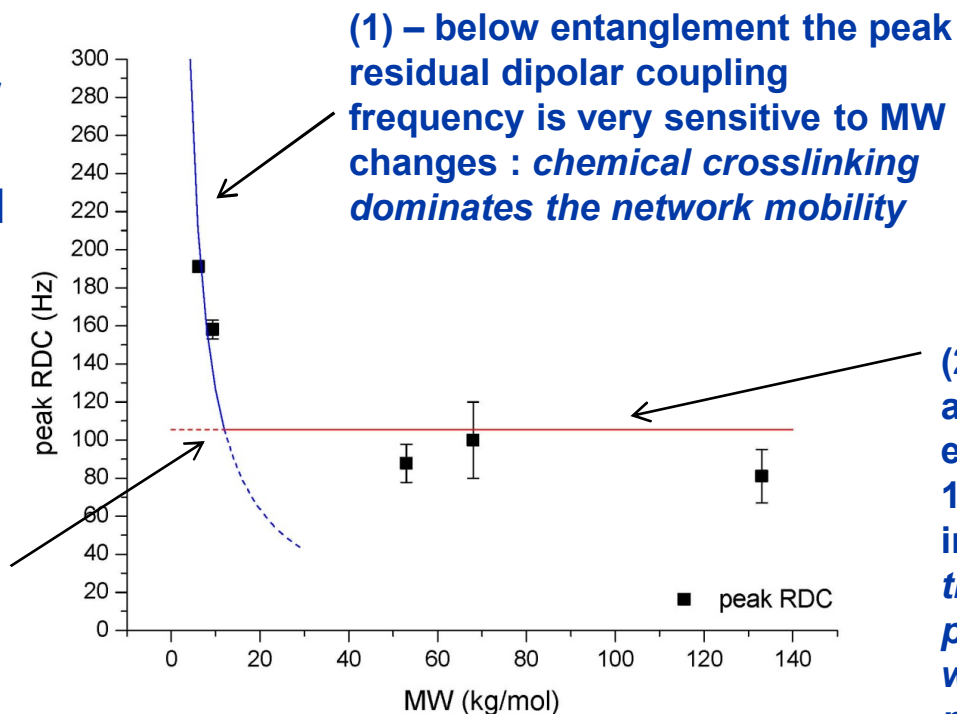


# MQ-NMR characterization: Monomodal systems

- The monomodal series, a (nominally) tetra-functionally crosslinked network with a series of end-end chain lengths of 8, 10, 31, 51, 68 & 133 KDa was analyzed using the prescribed NMR methodology

If we plot peak RDC values for each network vs. MW, a trend is apparent:

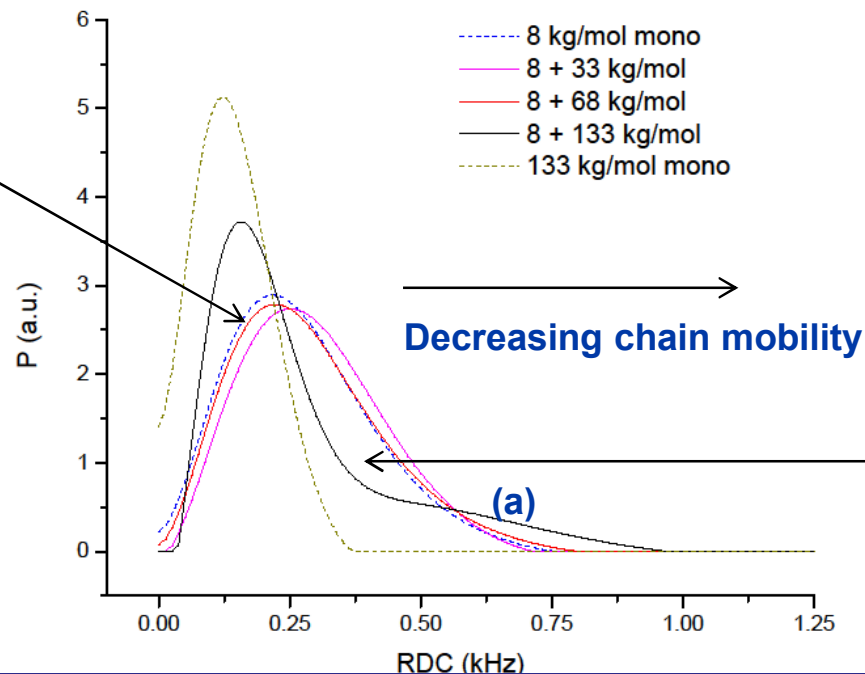
(3) – our experimental data (at this stage) correspond well with theory



# MQ-NMR characterization: Bimodal systems

- Here we have characterized the 1<sup>st</sup> series of bimodal networks, formulated with a 1:1 molar ratio of 8 KDa and 133KDa PDMS, tetra-functionally crosslinked. Shown below are the RDC distributions as a function of relative population

Up to a long chain mass of 68KDa it is apparent that the 8KDa (short chains) dominate the network properties : *Even long with chain lengths well above entanglement it is the short end-end chains which define the motional dynamics of the system*



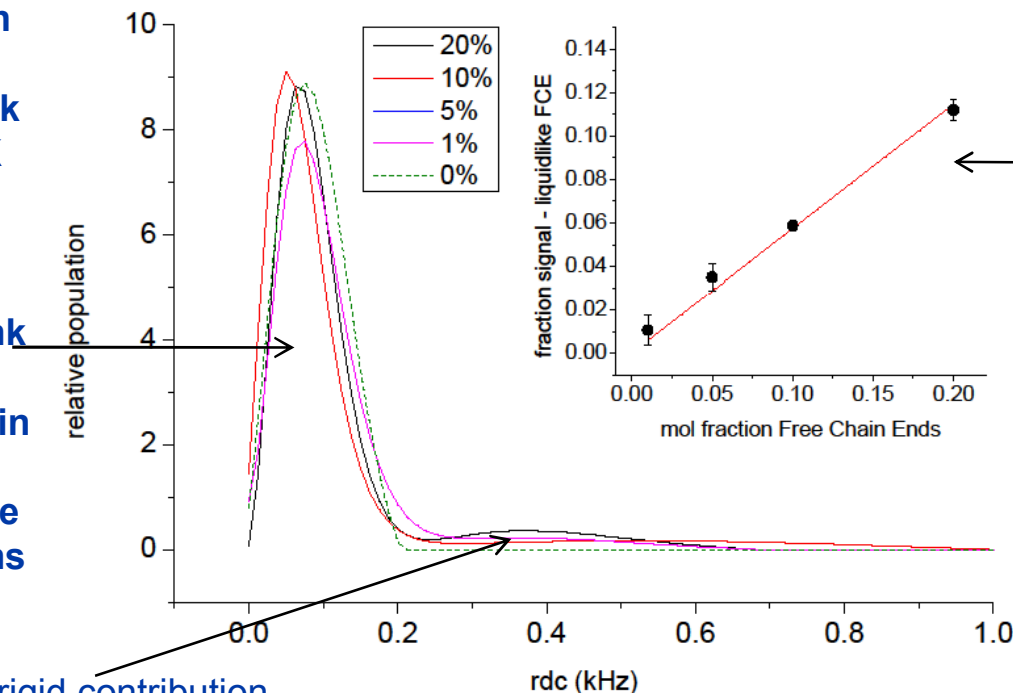
**Significantly, however – above ~70 KDa we see that the long chain segments start to influence the network properties: at high MW values, crosslink density is inevitably decreased. Importantly we also see the in-growth of a increasingly rigid component (a). This is the onset of true bimodality: the formation of two distinct populations of chains with**

The observation of a bimodal population and the mass range / high to low ratios over which it is observed is of significance and further correlates our experimental data with existing network theory

# NMR data: Controlled free chain end systems

- A final case is that of the monomodal (68KDa) networks incorporating 1-20 mol % of a 14KDa free chain ends

Again, we have the distributions of RDC values as a function of relative population. The bulk behavior of the 68K network appears to be generally insensitive to the decreasing crosslink density with increasing free-chain end levels – a trend we saw earlier in the monomodal systems



What is not shown directly in the RDC distribution curves is a secondary extracted contribution from extremely mobile 'liquid like' chains. This contribution has been quantified and is shown in the inset as a function of mol % free chain ends

*What we observe is the growth in a distinct population of extremely mobile, liquid-like chains i.e. we can observe & quantify the effects of the FCE's on the network properties*

There is also a small, rigid contribution from TEOS self condensation at high free chain end loadings





# In summary

- This work is at a relatively early stage, however it has been demonstrated that we can reliably probe basic network architectures using the MQ-NMR technique.
- The initial results are in good agreement with what is known from standard network theory and will serve as a basis for the study of progressively increasing structural complexity in Siloxane network systems



# Further work

- A move away from tin catalyzed condensation cured systems towards Pt mediated vinyl addition chemistry.
- Tri-modal networks, variable bi & tri modal chain ratios
- X-functional crosslinkers
- Filler contributions
- Solvent effects
- Aging and degradative effects
- Feeding our expanding experimental dataset into actual models of network behavior



# THANK YOU FOR YOUR ATTENTION

